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<b>(21) International Application Number:</b> PCT/US97/02534 <b>(22) International Filing Date:</b> 19 February 1997 (19.02.97) <b>(30) Priority Data:</b> 96870020.3 29 February 1996 (29.02.96) EP <b>(34) Countries for which the regional or international application was filed:</b> AT et al. <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HERBOTS, Ivan, Maurice, Alfons, Jan [BE/BE]; Hollegat 11, B-9230 Wetteren (BE). MOESE, Rosa, Laura [US/US]; 8815 Eagle Creek Court, West Chester, OH 45069 (US). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B-1840 Londerzeel (BE). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CLEANING COMPOSITIONS COMPRISING ENDO-DEXTRANASE  <b>(57) Abstract</b>  The present invention relates to cleaning compositions comprising an endo-dextranase enzyme, preferably an alkaline endo-dextranase, which provide improved specific or broad stain removal, enhanced overall cleaning performances and sanitisation of the treated surface together with malodour control.		

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## CLEANING COMPOSITIONS COMPRISING ENDO-DEXTRANASE

### FIELD OF THE INVENTION

The present invention relates to cleaning compositions including dishwashing, hard surface cleaning, toilet bowl cleaning, laundry and personal cleansing compositions, containing an endo-dextranase enzyme.

### BACKGROUND OF THE INVENTION

The overall performance of a cleaning product for use in washing or cleaning method such as dishwashing, hard surface cleaning, toilet bowl cleaning and laundry, is judged by a number of factors, including the ability to remove soils and the ability to prevent redeposition of the soils or the breakdown products of the soils on the articles in the wash.

Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange, tomato, banana, tea mango, spinach soils and grass. Also residues from plants usual contaminating inorganic compounds like mud or clay are very difficult to remove. The substrates can be dishes, hard surfaces, toilet bowls, skin, scalp, hair or fabrics.

Moreover, complex and high molecular weight carbohydrates structures are produced by natural microbial activity on stains and/or soils surfaces upon ageing. This complex and high molecular weight carbohydrates structures form a physical barrier and prevent effective removal of the stains and/or soils from the treated surfaces by active cleaning ingredients. Additionally such complex and high molecular weight carbohydrates structures form an ideal substrate for further

microbial development. Such complex and high molecular weight carbohydrates structures are represented by dextrans, being high molecular weight polysaccharides with a D-glucose backbone characterised by predominantly alpha-D(1-6) links.

It is therefore an object of the present invention to provide cleaning compositions which provide improved specific or broad stain removal, enhanced overall cleaning performance and sanitisation of the treated surface together with malodour control.

It has now been found that endo-dextranase is a carbohydrase enzyme which improves specific or broad stain removal, boosts overall cleaning performances and provides the sanitisation of the treated surfaces by degrading the complex and high molecular weight carbohydrates structures. During and after the enzymatic degradation of the high molecular weight carbohydrates, residual stains and/or soil components are exposed to the cleaning action of other cleaning active ingredients.

It has also been found that the combinations of endo-dextranase with selected cleaning ingredients as enzymes, bleaching agents and dye transfer inhibiting polymers provide enhanced stain removal and improved overall cleaning performance.

In addition, it has been found that endo-dextranase achieve the breakdown of highly viscous dextran-barriers of bacterial origin on the various stains surfaces achieving sanitisation and in the specific case of dishwashing and toilet bowl cleaning, endo-dextranases demonstrate high incidence on bacterial activity on ageing soiled dishes, solubilise bacterial "slime residue" in toilet bowls.

According to a preferred embodiment of the present invention, endo-dextranase can be incorporated in personal cleansing products. Generally, the performance of cleaning products for personal cleaning is judged by mild cleaning effect and sanitisation. It has been found that the addition of the endo-dextranase enzyme provides mild sanitization effects controlling the bacterial activity on the skin/scalp.

This mild sanitisation effects can be used to reduce or prevent inflammation of the sensitive skin, the formation of pimples and spots due to microbial activity in the skin-pores and for mild wound cleaning.

Dextranases are described in the prior art such as in contact lens cleaning applications (JP 30196724), in sweetening compositions (JP 4173070 - JP 1228467), in pharmaceutical applications as drug carrier (DD 255952 - WO 9401136) or for preparation of blood plasma extenders (US 5229277) and in biotechnology applications (JP 61141899 - JP 6284889 - DE 4216002).

Dextranases, including endo- and exo-dextranases, are commonly used in oral care. Dextranases are ingredients generally included in toothpaste, buccal composition, denture cleaner, tooth powder, mouth wash, troche, liquid or paste liniment or chewing gum which provide cleaning (JP 7069854), dental plaque inhibition (EP 524732 - US 5320830 - EP 411770), periodontal diseases treatment (JP 4182419 - EP 243002), tooth decay prevention (JP 3244377 - JP 61233609) and dental caries control (EP 524732 - SU 1521482 - JP 1034911).

However, benefits for the use of an endo-dextranase enzyme in cleaning formulations have not been previously recognised.

### SUMMARY OF THE INVENTION

The present invention relates to cleaning compositions comprising an endo-dextranase enzyme, preferably an alkaline endo-dextranase, which provide improved specific or broad stain removal, enhanced overall cleaning performances and sanitisation of the treated surfaces together with malodour control.

### DETAILED DESCRIPTION OF THE INVENTION

An essential component of the cleaning compositions of the invention is an endo-dextranase enzyme. This enzyme is incorporated into compositions at a level from  $10^{-6}\%$  to 1% and preferably from  $10^{-5}\%$  to 0.5% pure active enzyme by weight of total composition.

By endo-dextranase enzyme it is meant herein any enzyme which degrade, for instance hydrolyse and/or modify 1,6-alpha-glucosidic linkages in dextran based substrate; dextrans being high molecular weight polysaccharides with a D-glucose backbone characterised by predominantly alpha-D(1-6) links. Endo-dextranases can be of fungal origin e.g. Penicillium species or can be expressed in any other suitable host organism via cloning techniques known in the art. The naturally occurring endo-dextranase from Penicillium lilacinum is especially suited for incorporation in neutral pH or granular detergents.

A preferred endo-dextranase is an alkaline endo-dextranase. By the term "alkaline endo-dextranase" it is meant any endo-dextranase having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its optimum activity, at a pH ranging from 7 to 11 and covers preferably endo-dextranase having an optimum activity at a pH ranging from 7 to 11.

The production and properties of an alkaline dextranase from a *Brevibacterium* is provided in Agr. Biol. Chem. (1973), 37(11), 2527-33 and US 3, 737,383. Dextranases with increased pH stability are disclosed in Chem. Pharm. Bull. (1975) 23(12), 3223-7 and Chem. Pharm. Bull. (1974) 22(12), 2941-6.

Endo-dextranase enzymes herein include naturally derived endo-dextranase enzymes and any variants showing a positive immunological cross-reaction with an antibody directed against natural occurring endo-dextranase.

Any such variants may be specifically designed with regard to the optimisation of performance efficiency in the cleaning compositions of the invention. For example, variants may be designed

such that the compatibility of the enzyme to commonly encountered components of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

Endo-dextranase can be a carbohydrase from the following EC category: EC 3.2.1.11 and are commercialised by Sigma Chemicals, Fluka Fine Chemicals and Novo Nordisk.

The endo-dextranase activity is measured by the enzymatic assay for Dextranase according the Quality Control Test Procedure from the Sigma Chemicals Cie or the method described by J. Janson and J. Porathin, *Methods of Enzymology* VIII, 315 (1966). The dextran substrate (Molecular weight between 200,000 and 500,000) is degraded by the dextranase enzyme to form isomaltose during a 30 minutes incubation in 100 mM potassium phosphate buffer at pH 6.0 and a temperature of 37°C. Variations of this method include variation of incubation time, temperature and dextran molecular weight. One DU unit liberates 1 micro mole of isomaltose (measured as maltose) per minute at a pH 6.0 and a temperature of 37°C, using dextran as substrate.

According to the present invention, the endo-dextranase comprised into the cleaning compositions provides the sanitisation of the treated surfaces by degrading the complex and high molecular weight carbohydrates structures.

Sanitisation includes all positive effect obtained by the inhibition or reduction of microbial activity on fabrics and other surfaces, such as the prevention of malodour development and bacterial/fungal growth. For example, it provides prevention of malodour development on stored and weared fabrics, on stored dishware, especially plastic kitchen gear and in toilets. In particular, the composition of the invention will inhibit or at least reduce the bacterial and/or fungal development on moist fabric waiting for further laundry processing and thereby preventing the formation of malodour. In addition, bacterial and/or fungal growth on hard surfaces such as tiles and their silicone joints, sanitary installations, will be prevented. Moreover, it also has been found that the endo-dextranase enzyme is capable to control microbial activity on the human body.

Without being bound by theory, it is believed that the sanitisation occurs via the enzymatic degradation of the protective capsular carbohydrates of micro-organisms exposing them to the environment and to sanitising agents like surfactants and/or to chemicals sanitisers further comprised in the cleaning composition of the present invention.

The sanitisation potential of the cleaning compositions of the present invention can be enhanced by the addition of chemical sanitisers such as Triclosan and/or hexemidine. *Parfums Cosmétiques Actualités* No 125, Nov, 1995, 51-4 describes suitable chemical sanitisers.

The sanitisation benefits of the cleaning compositions of the present invention can be evaluated by the Minimum Inhibitory Concentration (MIC) as described in *Tuber. Lung. Dis.* 1994 Aug; 75(4):286-90; *J. Clin. Microbiol.* 1994 May; 32(5):1261-7 and *J. Clin. Microbiol.* 1992 Oct; 30(10):2692-7.

#### **DETERGENT COMPONENTS**



The cleaning compositions of the invention may also contain additional detergent components. The precise nature of these additional components and levels of incorporation thereof will depend on the physical form of the composition and the nature of the cleaning operation for which it is to be used.

The compositions of the invention may for example, be formulated as hand and machine dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions, and compositions for use in general household hard surface cleaning operations including toilet bowl cleaning and rim-block/in-tank block. Personal cleansing products also form part of the present invention. Compositions containing such endo-dextranase enzymes can also be formulated as sanitisation and malodour control products.

The cleaning compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. The compositions of the present invention can be incorporated into a spray dispenser as described in US 5,532,023 that can create an article of manufacture that can facilitate the cleaning and/or sanitisation of the surface treated. Granular compositions can also be in "compact" form, the liquid compositions can also be in a "concentrated" form.

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected

from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

The compositions of the invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

Such compositions containing endo-dextranase enzymes can provide fabric cleaning, stain removal, whiteness maintenance, softening, color appearance and dye transfer inhibition when formulated as laundry detergent compositions.

If needed the density of the laundry detergent compositions herein ranges from 550 to 1000 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition.

In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkalin -earth-metal salts of sulphates and chlorides.

A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents.

Typically the water content of the concentrated liquid detergent is less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

#### Conventional detergent enzymes

Preferred cleaning compositions of the present invention may further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, esterases, cutinases, pectinases, keratanase, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

Such combinations of endo-dextranase, preferably alkaline endo-dextranase, with other detergent enzymes will further boost cleaning by allowing more efficient access of other enzymes to the stains and/or soils. In particular, combinations with acid, neutral and alkaline proteases, keratanase, endo-glycosidases hydrolysing  $\alpha$ - or  $\beta$ -configured branched or linear polyglycosidic substrates with predominantly 1-3, 1-4 and 1-6 linked monomers,  $\alpha$ - and  $\beta$ -amylases, exo- and endo-cellulases, hemicellulases, endo- and exo-xylanases, endo- and exo-pectinases, hyaluronidase and chondroitinase hydrolysing glyco-proteininc substrates, lipases and wax-esterases hydrolysing fats and waxes.

A preferred combination is a cleaning composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Said cellulases are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of active enzyme by weight of the cleaning composition.

Combinations of endo-dextranase, preferably alkaline endo-dextranase with enzymatic bleach systems provide enhanced sanitisation and/or bleaching performance on a wider range of stains.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-p peroxidase. Peroxidase-containing detergent compositions are disclosed, for

example, in PCT International Applications WO 89/099813 and in European Patent applications EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621). Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the cleaning composition at levels from 0.0001% to 2%, preferably of active enzyme by weight of the cleaning composition.

It has been found that the combination of the endo-dextranase enzyme, preferably alkaline endo-dextranase with a protease enzyme provides enhanced specific or broad stain removal, improved overall cleaning performance and sanitisation of the treated surface with malodour control.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Nordisk A/S (Denmark), those sold under the tradename Maxatase, Maxacal, Maxapem and Properase by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Also proteases described in our co-pending application USSN 08/136,797 can be included in the cleaning composition of the invention. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Other preferred enzymes that can be included in the cleaning compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas

stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Especially suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup>(Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of active enzyme by weight of the cleaning composition.

Amylases (& and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl<sup>R</sup>, (Novo Nordisk), Fungamyl<sup>R</sup> and BAN<sup>R</sup> (Novo Nordisk).

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Said enzymes are normally incorporated in the cleaning composition at levels from 0.0001% to 2% of active enzyme by weight of the cleaning composition.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

**Bleach syst ms**

Combinations of endo-dextranases, preferably alkaline endo-dextranase with conventional bleach systems provide enhanced sanitisation and/or bleaching performance on a wider range of stains.

Such bleaching systems that can be included in the cleaning compositions of the present invention include bleaching agents such as PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%. In general, bleaching compounds are optional components in non-liquid formulations, e.g. granular detergents.

The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Applications 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy caproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at

0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylenediamine (TAED), nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.



Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

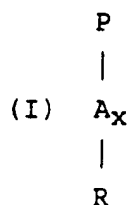
#### Polymeric dye transfer inhibiting agents

Combinations of endo-dextranase, preferably alkaline endo-dextranase with dye transfer inhibiting polymers providing results in improved withness maintenance and enhanced soil-releasing benefits.

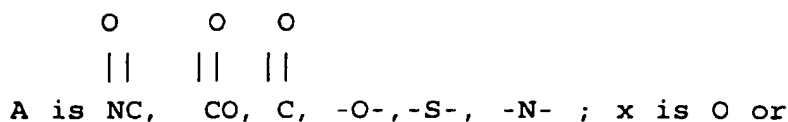
Therefore, cleaning compositions according to the present invention may also further comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into cleaning compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash. Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof. Addition of such polymers also enhances the performance of the enzymes according to the invention.

## a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :



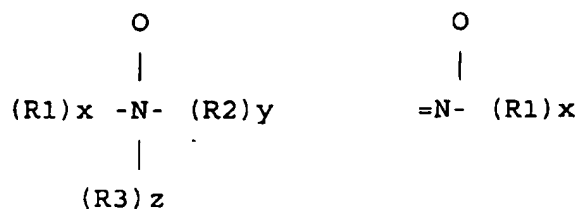
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.



1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a  $PK_a < 10$ , preferably  $PK_a < 7$ , more preferred  $PK_a < 6$ .

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

#### b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in cleaning compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer

has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000. The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization". Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith. The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

#### c) Polyvinylpyrrolidone

The cleaning compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

The cleaning compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The cleaning compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co-pending patent application 94870213.9

**Surfactant system**

The cleaning compositions according to the present invention generally comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 40% by weight of laundry and rinse added fabric softener compositions in accord with the invention.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Preferred non-alkylbenzene sulfonate surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkylphenol ethoxylates).

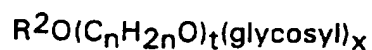
The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a



polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms;  $n$  is 2 or 3, preferably 2;  $t$  is from 0 to about 10, preferably 0; and  $x$  is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

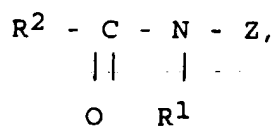
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to

increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula:



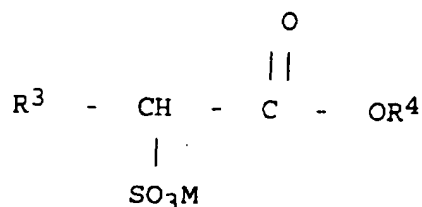
wherein  $R^1$  is H, or  $R^1$  is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof,  $R^2$  is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably,  $R^1$  is methyl,  $R^2$  is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

When included in such laundry detergent compositions, the nonionic surfactant systems of the present invention act to improve the greasy/oily stain removal properties of such laundry detergent compositions across a broad range of laundry conditions.

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula  $RO(A)_mSO_3M$  wherein R is an unsubstituted C<sub>10-24</sub> alkyl or hydroxyalkyl group having a C<sub>10-24</sub> alkyl component, preferably a C<sub>12-20</sub> alkyl or hydroxyalkyl, more preferably C<sub>12-18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxyated sulfates as well as alkyl propoxyated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C<sub>12-18</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12-18</sub>E(1.0)M), C<sub>12-18</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12-18</sub>E(2.25)M), C<sub>12-18</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12-18</sub>E(3.0)M), and C<sub>12-18</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12-18</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

Suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl pip rdinium cations and

quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g. below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the cleaning compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula  $RO(CH_2CH_2O)_k-CH_2COO-M^+$  wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

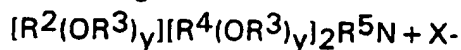
Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column

23, line 58 through Column 29, line 23 (herein incorporated by reference ).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

The cleaning compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the cleaning compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



wherein  $R^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $R^3$  is selected from the group consisting of  $-CH_2CH_2-$ ,  $-CH_2CH(CH_3)-$ ,  $-CH_2CH(CH_2OH)-$ ,  $-CH_2CH_2CH_2-$ , and mixtures thereof; each  $R^4$  is selected from the group consisting of  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, benzyl ring structures formed by joining the two  $R^4$  groups,  $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$  wherein  $R^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when  $y$  is not 0;  $R^5$  is the same as  $R^4$  or is an alkyl chain wherein the total number of carbon atoms of  $R^2$  plus  $R^5$  is not more than about 18; each  $y$  is from 0 to about 10 and the sum of the  $y$  values is from 0 to about 15; and  $X$  is any compatible anion.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein  $R_1$  is  $C_8$ - $C_{16}$  alkyl, each of  $R_2$ ,  $R_3$  and  $R_4$  is independently  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxy alkyl, benzyl, and  $-(C_2H_4O)_xH$  where  $x$  has a value from 2 to 5, and  $X$  is an anion. Not more than one of  $R_2$ ,  $R_3$  or  $R_4$  should be benzyl.

The preferred alkyl chain length for  $R_1$  is  $C_{12}$ - $C_{15}$  particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for  $R_2R_3$  and  $R_4$  are methyl and hydroxyethyl groups and the anion  $X$  may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;  
 coconut methyl dihydroxyethyl ammonium chloride or bromide;  
 decyl triethyl ammonium chloride;  
 decyl dimethyl hydroxyethyl ammonium chloride or bromide;  
 $C_{12-15}$  dimethyl hydroxyethyl ammonium chloride or bromide;  
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;  
 myristyl trimethyl ammonium methyl sulphate;  
 lauryl dimethyl benzyl ammonium chloride or bromide;  
 lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;  
 choline esters (compounds of formula (i) wherein  $R_1$  is

$CH_2-CH_2-O-C-C_{12-14}$  alkyl and  $R_2R_3R_4$  are methyl).



di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

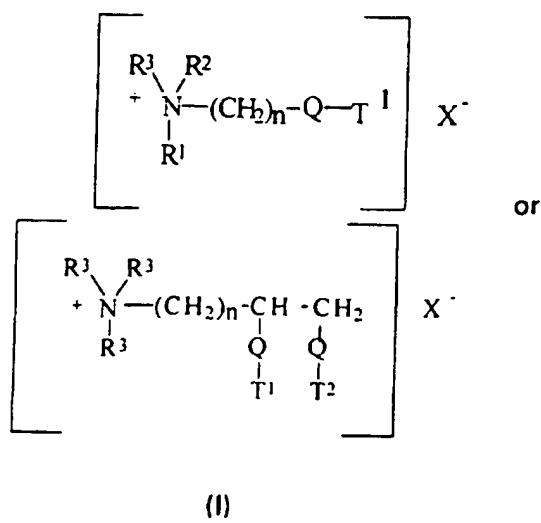
Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C<sub>12-14</sub> alkyl hydroxyethyl dimethylammonium chloride;
- 11) C<sub>12-18</sub> alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallowoyloxyethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :





wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR<sup>4</sup>-C(O)-, -C(O)-NR<sup>4</sup>-;

R<sup>1</sup> is (CH<sub>2</sub>)<sub>n</sub>-Q-T<sup>2</sup> or T<sup>3</sup>;

R<sup>2</sup> is (CH<sub>2</sub>)<sub>m</sub>-Q-T<sup>4</sup> or T<sup>5</sup> or R<sup>3</sup>;

R<sup>3</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl or H;

R<sup>4</sup> is H or C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl;

T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> are independently C<sub>11</sub>-C<sub>22</sub> alkyl or alkenyl;

n and m are integers from 1 to 4; and

X<sup>-</sup> is a softener-compatible anion.

Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
  - 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
  - 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
  - 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
  - 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
  - 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
  - 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
  - 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the cleaning compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably

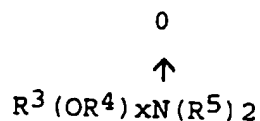
from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein  $R^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $R^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides and  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

#### **Builder system**

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenylsuccinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacar-

boxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the cleaning compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include  $\text{Na}_2\text{EDDS}$  and  $\text{Na}_4\text{EDDS}$ . Examples of such preferred magnesium salts of EDDS include  $\text{MgEDDS}$  and  $\text{Mg}_2\text{EDDS}$ . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with malic anhydride, such

copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 10% to 70% and most usually from 10% to 60% by weight.

#### **Suds suppressor**

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R. Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8.

Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil<sup>R</sup>.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

#### **Color care benefits**

Combinations with technologies which also provide a type of color care benefit can also be used. Examples of these technologies are metallo catalysts for color maintenance. Such metallo catalysts are described in the European patent EP 0 596 184 and in the copending European Patent Application No. 94870206.3.

#### **Other detergent ingredients**

Other components used in cleaning compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

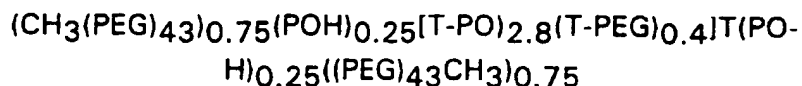


Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or copolymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-sodium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or copolymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is  $-(\text{OC}_2\text{H}_4)_n\text{O}-$ , PO is  $(\text{OC}_3\text{H}_6\text{O})$  and T is  $(\text{pOC}_6\text{H}_4\text{CO})$ .

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

#### Softening agents

Fabric softening agents can also be incorporated into cleaning compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-O 026 527 and EP-B-O 026 528 and di-long-chain amides as disclosed in EP-B-O 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-O 299 575 and O 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

#### Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5 °C to 95 °C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11.

A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres.

According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

A non-alkaline endo-dextranase and/or an alkaline endo-dextranase such as described in Agr. Biol. Chem. (1973), 37(11), 2527-33 and US 3,737,383, will be added to the following compositions illustrated below at a level from 10<sup>-6</sup>% to 1% preferably from 10<sup>-5</sup>% to 0.5% pure enzyme by weight of total composition.

In the cleaning compositions, the abbreviated component identifications have the following meanings:

LAS : Sodium linear C<sub>12</sub> alkyl benzene sulphonate

TAS	: Sodium tallow alkyl sulphate
XYAS	: Sodium C <sub>1X</sub> - C <sub>1Y</sub> alkyl sulfate
SAS	: C <sub>12</sub> -C <sub>14</sub> secondary (2,3) alkyl sulfate in the form of the sodium salt.
APG	: Alkyl polyglycoside surfactant of formula C <sub>12</sub> - (glycosyl) <sub>x</sub> , where x is 1.5,
AEC	: Alkyl ethoxycarboxylate surfactant of formula C <sub>12</sub> ethoxy (2) carboxylate.
SS	: Secondary soap surfactant of formula 2-butyl octanoic acid
25EY	: A C <sub>12</sub> -C <sub>15</sub> predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
45EY	: A C <sub>14</sub> - C <sub>15</sub> predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEZX	: C <sub>1X</sub> - C <sub>1Y</sub> sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
Nonionic	: C <sub>13</sub> -C <sub>15</sub> mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafax LF404 by BASF GmbH
CFAA	: C <sub>12</sub> -C <sub>14</sub> alkyl N-methyl glucamide

TFAA	: C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide.
Silicate	: Amorphous Sodium Silicate (SiO <sub>2</sub> :Na <sub>2</sub> O ratio = 2.0)
NaSKS-6	: Crystalline layered silicate of formula $\delta$ -Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
Carbonate	: Anhydrous sodium carbonate
Phosphate	: Sodium tripolyphosphate
MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Polyacrylate	: Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
Zeolite A	: Hydrated Sodium Aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> · 27H <sub>2</sub> O having a primary particle size in the range from 1 to 10 micrometers
Zeolite MAP	: Alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33
Citrate	: Tri-sodium citrate dihydrate
Citric	: Citric Acid
Perborate	: Anhydrous sodium perborate monohydrate bleach, empirical formula NaBO <sub>2</sub> · H <sub>2</sub> O <sub>2</sub>
PB4	: Anhydrous sodium perborate tetrahydrate

- Percarbonate** : Anhydrous sodium percarbonate bleach of empirical formula  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
- TAED** : Tetraacetyl ethylene diamine
- Paraffin** : Paraffin oil sold under the tradename Winog 70 by Wintershall.
- Pectinase** : Pectolytic enzyme sold under the tradename Pectinex AR by Novo Nordisk A/S.
- Xylanase** : Xylanolytic enzyme sold under the tradenames Pulpzyme HB or SP431 by Novo Nordisk A/S or Lyxasan (Gist-Brocades) or Optipulp or Xylanase (Solvay).
- Protease** : Proteolytic enzyme sold under the tradename Savinase, Alcalase, Maxacal by Novo Nordisk A/S and proteases described in patents WO91/06637 and/or US429882.
- Amylase** : Amylolytic enzyme sold under the tradename Termamyl by Novo Nordisk A/S
- Lipase** : Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S
- Peroxidase** : Peroxidase enzyme
- Cellulase** : Cellulosic enzyme sold under the tradename Carezyme or Celluzyme by Novo Nordisk A/S.
- CMC** : Sodium carboxymethyl cellulose

- HEDP : 1,1-hydroxyethane diphosphonic acid
- DETPMP : Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
- PVP : Polyvinyl pyrrolidone polymer
- EDDS : Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt.
- Suds Suppressor : 25% paraffin wax Mpt 50°C, 17% hydrophobic silica, 58% paraffin oil.
- Granular Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form
- SCS : Sodium cumene sulphonate
- Sulphate : Anhydrous sodium sulphate.
- HMWPEO : High molecular weight polyethylene oxide
- PGMS : Polyglycerol monostearate having a tradename of Radasurf 248



TAE 25 : Tallow alcohol ethoxylate (25)

### Example 1

The following machine dishwashing detergent compositions were prepared (parts by weight) in accord with the invention.

	I	II	III	IV	V	VI
Citrate	24.0	-	-	24.0	24.0	29.0
Phosphate	-	30.0	46.0	-	-	-
MA/AA	6.0	-	-	6.0	6.0	-
Silicate	27.5	-	33.0	27.5	27.5	25.7
Carbonate	12.5	23.5	-	12.5	12.5	-
Perborate	10.4	10.4	10.4	10.4	10.4	1.9
PB4	-	-	-	-	-	8.7
TAED	3.0	3.0	3.0	3.0	3.0	4.4
Benzotriazole	-	0.3	-	-	-	0.3
Paraffin	-	0.5	-	-	-	0.5
HEDP	-	-	-	-	-	0.5
Protease	0.04	0.04	0.04	0.04	0.04	0.04
Amylase	-	0.01	0.01	0.02	0.01	0.02
Lipase	-	-	0.03	0.03	0.03	-
Xylanase	-	-	0.04	-	0.01	0.05
Nonionic	-	1.5	1.5	1.5	1.5	1.5
Sulphate	1.4	2.4	2.4	12.1	12.1	3.0
35AE3S	-	-	5.0	-	5.0	-
Granular Suds	1.0	-	-	-	-	-
Suppressor						
Water & minors	Up to					
	100%					

The compositions provide good soil removal when used in a machine dishwashing process.

### Example 2

The following liquid manual dishwashing compositions were prepared in accord with the invention. The pH of the compositions was adjusted to be in the range 7.0 to 7.4.

	<u>% by weight</u>				
	I	II	III	IV	V
LAS	-	-	-	-	10.0
23AE0.8S	10.0	10.0	6.0	5.0	5.0
23AE3S	3.0	7.0	10.0	15.0	-
SS	-	-	4.0	-	-
C12/14 alkyl amine oxide	2.0	1.0	-	1.0	2.0
AEC	-	-	-	5.0	-
C12/14 alkyl di methyl betaine	-	1.0	1.5	2.0	-
C12/14 Ampholak(TM)	-	-	1.5	-	-
CFAA	12.0	-	12.0	11.0	-
APG	-	12.0	-	-	-
C10 Alkyl Ethoxylate (ave. 8)	5.0	5.0	5.0	4.6	5.0
Mg <sup>++</sup> ion	-	0.6	0.3	0.3	0.6
Ca <sup>++</sup> ion	0.05	0.05	0.3	0.15	0.1
Maleic acid	-	-	0.2	0.3	-
Boric acid	1.0	1.0	1.0	2.0	2.0
Formic acid	1.0	1.0	1.0	-	-
Protease	0.01	0.02	0.01	0.02	0.03
Amylase	-	0.01	-	0.01	0.01
Lipase	-	-	0.01	0.02	-
Pectinase	-	-	-	0.01	-
Xylanase	-	-	0.02	0.03	-

Water &amp; minors

Up to 100%

Example 3

Granular fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV	V
LAS	22.0	22.0	22.0	22.0	22.0
Phosphate	23.0	23.0	23.0	23.0	23.0
Carbonate	23.0	23.0	23.0	23.0	23.0
Silicate	14.0	14.0	14.0	14.0	14.0
Zeolite A	8.2	8.2	8.2	8.2	8.2
DETPMP	0.4	0.4	0.4	0.4	0.4
Sodium Sulfate	5.5	5.5	5.5	5.5	5.5
Protease	0.01	0.02	0.01	0.005	.
Lipase	0.005	0.01	.	0.01	.
Cellulase	0.001	.	.	0.001	.
Amylase	0.01	.	0.01	0.006	.
Pectinase	0.02	0.02	0.02	.	.
Water/minors	Up to 100%				

Example 4

Granular fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III	IV
LAS	14.0	14.0	14.0	14.0
Zeolite A	26.0	26.0	26.0	26.0
SS	5.0	5.0	5.0	5.0
SAS	6.0	6.0	6.0	6.0

50

Citrate	5.0	5.0	5.0	5.0
Sodium Sulfate	18.0	18.0	18.0	28.0
Perborate	17.0	17.0	17.0	-
TAED	5.5	5.5	5.5	-

	I	II	III	IV
Protease	0.06	0.03	0.02	0.08
Lipase	-	0.01	0.005	0.01
Cellulase	-	-	0.001	0.001
Amylase	-	0.01	0.01	0.005
Pectinase	-	-	0.02	0.01
Xylanase	-	-	0.02	-
Water/minors		Up to 100%		

Example 5

Granular fabric cleaning compositions in accord with the invention which are especially useful in the laundering of coloured fabrics were prepared as follows :

	I	II	III	IV
LAS	11.4	10.7	.	.
TAS	1.8	2.4	.	.
TFAA	.	.	4.0	4.0
45AS	3.0	3.1	10.0	10.0
45E7	4.0	4.0	.	.
25E3S	.	.	3.0	3.0
68E11	1.8	1.8	.	.
25E5	.	.	8.0	8.0
Citrate	14.0	15.0	7.0	7.0
Carbonate	.	.	10	10
Citric acid	3.0	2.5	3.0	3.0
Zeolite A	32.5	32.1	25.0	25.0
Na-SKS-6	.	.	9.0	9.0
MA/AA	5.0	5.0	5.0	5.0
DETPMP	1.0	0.2	0.8	0.8

Protease	0.02	0.02	0.01	0.01
Lipase	0.03	0.04	0.005	0.005
Amylase	-	0.03	0.005	0.005
Silicate	2.0	2.5	-	-

	I	II	III	IV
Sulphate	3.5	5.2	3.0	3.0
PVP	0.3	0.5	-	-
Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone	-	-	0.2	0.2
Perborate	0.5	1.0	-	-
Percarbonate	-	-	0.5	1.0
Peroxidase	0.01	0.01	0.01	0.01
10-Phenothiazinepropionic acid	-	0.2	0.1	-
Phenol sulfonate	0.1	-	-	0.2
Water/Minors		Up to 100%		

**Example 6**

Granular fabric cleaning compositions in accord with the invention were prepared as follows:

	I	II	III
LAS	6.5	8.0	8.0
Sulfate	15.0	18.0	18.0
Zeolite A	26.0	22.0	22.0
Sodium nitrilotriacetate	5.0	5.0	5.0
PVP	0.5	0.7	0.7
TAED	3.0	3.0	3.0
Boric acid	4.0	-	-
Perborate	0.5	1.0	1.0
Phenol sulphonate	0.1	0.2	0.2

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10- Phenothiazinepropionic acid	-	-	0.2
Silicate	5.0	5.0	5.0
Carbonate	15.0	15.0	15.0
	I	II	III
Protease	0.0	0.0	0.0
Peroxidase	0.1	0.1	0.1
Lipase	0.0	0.0	0.0
Amylase	0.0	0.0	0.0
Xylanase	0.0	0.0	0.0
Cellulase	-	0.0	0.0
Water/minors	Up to 100%		

Example 7

A compact granular fabric cleaning composition in accord with the invention was prepared as follows:

45AS	8.0
25E3S	2.0
25E5	3.0
25E3	3.0
TFAA	2.5
Zeolite A	17.0
NaSKS-6	12.0
Citric acid	3.0
Carbonate	7.0
MA/AA	5.0
CMC	0.4
Poly (4-vinylpyridine)-N-oxide/ copolymer of vinylimidazole and vinylpyrrolidone	0.2
Protease	0.05
TAED	6.0
Percarbonat	22.0

EDDS	0.3
Granular suds suppressor	3.5
water/minors	Up to 100%

Example 8

A granular fabric cleaning compositions in accord with the invention which provide "softening through the wash" capability were prepared as follows:

	I	II
45AS	-	10.0
LAS	7.6	-
68AS	1.3	-
45E7	4.0	-
25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
Perborate	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.02	0.001
Silicate	3.0	5.0
Carbonate	10.0	10.0
Granular suds suppressor	1.0	4.0

CMC

0.2

0.1

Water/minors

Up to 100%

**Example 9**

Heavy duty liquid fabric cleaning compositions suitable for use in the pretreatment of stained fabrics and for use in a machine laundering method, in accord with the invention were prepared as follows:

	I	II	III	IV	V
24AS	20.0	20.0	20.0	20.0	20.0
SS	5.0	5.0	5.0	5.0	5.0
Citrate	1.0	1.0	1.0	1.0	1.0
12E <sub>3</sub>	13.0	13.0	13.0	13.0	13.0
Monethanolamine	2.5	2.5	2.5	2.5	2.5
Boric acid	2.75	2.75	1.5	1.5	1.5
Formic acid	-	-	1.0	1.0	1.0
Protease	0.005	0.03	0.02	0.04	0.01
Lipase	0.002	0.01	0.02	-	0.004
Amylase	0.005	0.005	-	-	0.004
Cellulase	-	-	0.01	-	0.01
Pectinase	-	0.02	-	-	0.02
Xylanase	-	-	-	-	0.03
Water/propylene glycol/ethanol (100:1:1)					

**Example 10**

Heavy duty liquid fabric cleaning compositions in accord with the invention were prepared as follows:

I II III IV



LAS acid form	-	-	25.0	-
C <sub>12-14</sub> alkenyl succinic acid	3.0	8.0	10.0	-
Citric acid	10.0	15.0	2.0	2.0
25AS acid form	8.0	8.0	-	15.0
25AE2S acid form	-	3.0	-	4.0
25AE7	-	8.0	-	6.0
	I	II	III	IV
25AE3	8.0	-	-	-
CFAA	-	-	-	6.0
DETPMP	0.2	-	1.0	1.0
Fatty acid	-	-	-	10.0
Oleic acid	1.8	-	1.0	-
Ethanol	4.0	4.0	6.0	2.0
Propanediol	2.0	2.0	6.0	10.0
Boric acid	2.75	2.75	2.75	2.75
Protease	0.02	0.02	0.02	0.01
Lipase	0.01	0.005	-	0.01
Amylase	0.005	0.01	-	0.01
Cellulase	0.005	-	-	-
Pectinase	0.02	-	-	-
Xylanase	0.05	-	-	-
Peroxidase	-	0.01	-	-
Coco-alkyl dimethyl hydroxy ethyl ammonium chloride	-	-	3.0	-
Smectite clay	-	-	5.0	-
PVP	1.0	2.0	-	-
Perborate	-	1.0	-	-
Phenol sulphonate	-	0.2	-	-
NaOH		Up to pH 7.5		
Waters/minors		Up to 100%		

Example 11

The following rinse added fabric softener composition was prepared in accord with the invention.

	I	II
Softener active	24.5	20.0
PGMS	2.0	-
TAE 25	1.5	-
Amylase	-	0.001
	I	II
Cellulase	0.001	0.001
HCL	-	0.03
Citrate	0.12	-
Antifoam agent	0.019	0.01
Blue dye	80ppm	25ppm
CaCl <sub>2</sub>	0.35	0.20
Perfume	0.90	0.90
Water and minors		Up to 100%

#### Example 11(b)

The following fabric softener composition was prepared in accord with the present invention :

	I	II	III
DEQA	2.6	19.0	-
SDASA	-	-	70.0
Stearic acid of IV = 0	0.3	-	-
Neodol 45-13	-	-	13.0
Hydrochloride acid	0.02	0.02	-
Ethanol	-	-	1.0

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PEG	-	0.6	-
Perfume	1.0	1.0	0.75
Digeranyl Succinate	-	-	0.38
Silicone antifoam	0.01	0.01	-
Electrolyte	-	600ppm	-
Dye	100ppm	50ppm	0.01
Water and minors	100%	100%	

Example 12

The following liquid hard surface cleaning compositions were prepared in accord with the present invention.

	I	II
Protease	0.01	0.02
Lipase	-	0.03
Amylase	-	0.01
Boric acid	2.75	2.75
NaC <sub>12</sub> Alkyl-benzene sulfonate	1.95	-
NaC <sub>12</sub> alkylsulfate	-	2.20
NaC <sub>12</sub> (ethoxy) * sulfate	-	2.20
C <sub>12</sub> dimethylamine oxide	-	0.50
Na Cumene sulfonate	1.30	-
Hexyl Carbitol *	6.30	6.30
Water/minors **	Up to 100%	

\* Diethyleneglycol monohexyl ether

\*\* All formulas adjusted to pH 7

Example 13

The following spray composition for cleaning hard surfaces and removing household mildew was prepared in accord with the present invention.

Amylase	0.01
Lipase	0.01
Sodium octyl sulfate	2.00
Sodium dodecyl sulfate	4.00
Sodium hydroxide	0.80
Silicate (Na)	0.04
Perfume	0.35

Water/minors

up to 100%

Example 14

The following bar fabric cleaning composition was prepared in accord with the present invention.

Protease	0.03
Lipase	0.01
Amylase	0.05
C <sub>12</sub> -C <sub>16</sub> alkyl sulfate, Na	20.0
C <sub>12</sub> -C <sub>14</sub> N-methyl glucamide	5.0
C <sub>11</sub> -C <sub>13</sub> alkyl benzene sulfonate, Na	10.0
Sodium carbonate	25.0
Sodium pyrophosphate	7.0
Sodium tripolyphosphate	7.0
Zeolite A	5.0
Carboxymethylcellulose	0.2
Polyacrylate (MW 1400)	0.2
Coconut monethanolamide	5.0
Brightener, perfume	0.2
CaSO <sub>4</sub>	1.0
MgSO <sub>4</sub>	1.0
Filler*	Balance to 100%

\* Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay (Kaolinite, Smectite), silicates and the like.

Example 15

The following lavatory cleansing block compositions were prepared in accord with the present invention.

	I	II	III
C16-18 fatty alcohol/50EO	80.0	.	.
LAS	.	.	80.0
Nonionic	.	1.0	.

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Oleoamide surfactant		26.0	
	I	II	III
Partially esterified copolymer of vinylmethyl ether and maleic anhydride, viscosity 0.1-0.5	5.0		
Polyethylene glycol MW 8000		39.0	
Water-soluble K-polyacrylate MW 4000-8000		12.0	
Water-soluble Na-copolymer of acrylamide (70%) and acrylic acid (30%) low MW		19.0	
Na triphosphate	10.0		
Carbonate			8.0
Dye	2.5	1.0	1.0
Perfume	3.0		7.0
KOH / HCL solution		pH 6-11	

Example 16

The following toilet bowl cleaning composition was prepared in accord with the present invention.

	I	II
C14-15 linear alcohol 7EO	2.0	10.0
Citric acid	10.0	5.0
DETPMP	-	1.0
Dye	2.0	1.0
Perfume	3.0	3.0
NaOH	pH 6-11	
Water and minors	Up to 100%	

Example 17

A liquid personal cleansing composition containing soap was prepared in accord with the present invention :

	I	II
Protease	0.10	-
Soap (K or Na)	15.00	-
30% Laurate		-
30% Myristate		-
25% Palmitate		-
15% Stearate		-
Fatty acids (above ratios)	4.50	-
Na Lauryl Sarcosinate	6.00	-
Sodium Laureth Sulfate	0.66	12.0
Cocamidopropylbetaine	1.33	3.0
Glycerine	15.00	-
Propylene Glycol	9.00	-
Ethylene glycol distearate (EDTA)	1.50	0.38
Cocoamide MEA	-	0.2
Perfume	-	0.6
*Polyquaterium-7	-	0.08
DMDM hydantoin	-	0.14
Sodium benzoate	-	0.25
Tetrasodium EDTA dihydrate	-	0.11
Citric	-	0.09
Propylparaben	0.10	-
Methylparaben	0.20	-
Calcium sulfate	3	-
Acetic acid	3	-
Water and minors	Up to 100%	
KOH/NaOH (pH adjustment)		6-11
* Copolymer of dimethyl dialkyl ammonium chloride and acrylamide		

#### Example 18

A personal cleansing bar composition was prepared in accord with the present invention :

Sodium Cocoyl Isethionate	47.20
Sodium Cetearyl sulfate	9.14
Paraffin	9.05
Sodium Soap (in situ)	3.67
Sodium Isethionate	5.51
Sodium Chloride	0.45
Titanium Dioxide	0.4
Trisodium EDTA	0.1
Trisodium Etidronate	0.1
Perfume	1.20
Na <sub>2</sub> SO <sub>4</sub>	0.87
Protease	0.10
Water	Balance to 100

#### Example 19

A shampoo composition was prepared in accord with the present invention :

	I	II	III	IV	V	VI
NH <sub>4</sub> laureth-3 sulfate /EDTA	16.0	18.0	10.0	16.0	14.0	18.0
NH <sub>4</sub> lauryl sulfate/EDTA	5.0	6.0	3.0	3.0	4.0	6.0
Na lauryl sarcosinate	-	-	2.0	-	-	-
Cocoamide MEA	1.0	-	-	1.0	0.6	-
Dimethicone 40/60	0.8	1.0	0.4	3.0	2.0	1.0
Polyquaternium-10	-	-	0.01	-	0.2	-
Cetyl alcohol	0.5	0.4	-	0.4	0.4	0.1
Stearyl alcohol	-	0.2	-	0.5	0.1	0.2
Panthenyl ethyl ether	0.2	-	-	0.2	0.2	0.2
Panthenol 10%	-	0.03	-	0.03	-	-
Tallow	-	-	-	-	-	0.5
Mineral oil	-	-	-	-	0.5	-
Tetrasodium EDTA	0.09	0.09	0.07	0.09	0.09	0.09



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DMDM Hydantoin	0.14	0.14	0.14	0.12	0.14	0.14
Sodium benzoate	0.25	0.25	-	0.25	0.25	0.25
Citrate	1.0	-	-	1.0	1.0	-

	I	II	III	IV	V	VI
Citric	0.1	-	0.3	0.1	-	-
Sodium hydroxide	-	-	0.3	-	-	-
Sodium phosphate	-	0.6	-	-	-	0.6
Disodium phosphate	-	0.2	-	-	-	0.2
62	1.5	1.5	3.0	1.5	2.0	1.5
Sodium chloride						
PEG-12	-	-	0.15	-	-	0.4
NH4 xylene sulfonate	0.4	0.4	-	0.4	0.4	0.4
Glycol distearate	1.0	3.0	1.5	2.0	3.0	0.5
Zinc pyrithione	-	-	1.0	-	-	-
Perfume	0.2	0.6	0.6	0.2	0.4	0.6
Water and minors			Up to 100%			

WHAT IS CLAIMED IS:

1. A cleaning composition comprising an endo-dextranase enzyme.
2. A cleaning composition according to claim 1 wherein said endo-dextranase has an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its optimum activity, at a pH ranging from 7 to 11.
3. A cleaning composition according to claims 1 and 2 wherein said endo-dextranase has an optimum activity at a pH ranging from 7 to 11.
4. A cleaning composition according to claims 1-3 wherein said endo-dextranase is present at a level from  $10^{-6}\%$  to 1% preferably from  $10^{-5}\%$  to 0.5% pure enzyme by weight of total composition.
5. A cleaning composition according to any of the preceding claims further comprising an enzyme selected from the group of cellulase, peroxidase, protease, amylase, lipase, cutinase or mixtures thereof.
6. A cleaning composition according claim 5 wherein said enzyme is a protease.
7. A cleaning composition according to any of the preceding claims further comprising a bleach activator and a bleaching agent.
8. A cleaning composition according to claim 7 wherein said bleaching agent is perborate or percarbonate.
9. A cleaning composition according to claims 7-8 comprising a peroxidase and 10-Phenothiazinepropionic acid as bleach activator.

10. A cleaning composition according to any of the preceding claims further comprising a dye transfer inhibiting polymer.
11. A cleaning composition according to any of the preceding claims further comprising a chemical sanitiser.
12. A cleaning composition according to any of the preceding claims characterised in that said composition is in the liquid, paste, gel, bar, tablets, powder, spray or granular form.
13. A detergent additive comprising an endo-dextranase enzyme.
14. A detergent additive according to claim 13 wherein said endo-dextranase has an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its optimum activity, at a pH ranging from 7 to 11.
15. A detergent additive according to claims 13 and 14 wherein said endo-dextranase has an optimum activity at a pH ranging from 7 to 11.
16. Use of an endo-dextranase in a cleaning composition for fabric cleaning and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric softening and/or fabric color appearance and/or dye transfer inhibition and/or fabric sanitisation.
17. Use of an endo-dextranase in a cleaning composition for cleaning and/or sanitisation of hard surfaces such as floors, walls, bathroom tiles, toilet bowls and dishes.
18. Use of an endo-dextranase in a personal cleansing composition.
19. Use of an endo-dextranase in a cleaning composition for inhibiting/reduction of fungal/bacterial development and/or for prevention of malodour formation.

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 97/02534

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D C12N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 710 313 A (MIYAJIMA NOBUYUKI ET AL) 1 December 1987 see abstract see example 9	1
A	US 4 011 169 A (DIEHL FRANCIS LOUVAINE ET AL) 8 March 1977 see abstract see column 4, line 4 see column 16, line 19	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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# INTERNATIONAL SEARCH REPORT

Inter national Application No  
PCT/US 97/02534

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>EP 0 382 020 A (HENKEL KGAA) 16 August 1990 see abstract</p> <p>---</p>	1
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